Determination of Trace Potassium in Concentration Salt Solution by Anti-Fluorescence Quenching Method on Rhodamine B-Sodium Tetraphenylborate System

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It is found that sodium tetraphenylborate had the ability to quench the fluorescence of Rhodamine B, could make the intensity of fluorescence weak or even disappear. But K^+, which can reacted with the sodium tetraphenylborate to form precipitation had the anti-quenching effect on Rhodamine B-sodium tetraphenylborate system, enhanced the intensity of fluorescence. The fluorescent signal enhancement degree was proportional to the concentration of K^+. Using antifluorescence quenching method, with 375 nm for excitation wavelength and 640 nm for emission wavelength, the fluorescence intensity F_1 and F_0 of solution and blank solution were measured. The different value $\Delta F = F_1-F_0$ was proportional to the concentration of K^+. Based on these, a new, simple and sensitive antifluorescence quenching method for determination of K^+ was established. The linear relationship between the different value ΔF of the intensity of fluorescence and the concentration of K^+ is in the range of 2.14 mg L^{-1}-43.0 mg L^{-1}. The detection limit is 0.642 mg L^{-1} and the relative standard deviation is 1.32 %. This method can be used for determination of trace potassium in concentration salt solution and has been successfully applied to determination of K^+ in common salt and compound sodium chloride injection with satisfactory results.

Key Words: Potassium, Rhodamine B-sodium tetraphenylborate system, Anti-fluorescence quenching, Concentration salt Solution.

INTRODUCTION

Potassium existed in human cells and tissues in the form of ions is an essential nutrition elements. It plays an important role in human physiology for maintaining the body's water balance and acid-base balance, regulating osmotic pressure *in vivo*. Myocardium and neuromuscular also need to have a relatively constant concentration of potassium ions to maintain the normal stress. Since there is no body organs for long-term storage of potassium, the potassium needed of the body must be constantly supplemented through adding food or infusion, balanced between the absorbed potassium and the digested potassium and maintained the body's normal growth and health. However, excessive intake of potassium, causes the hyperkalemia. The determination of K^+ in common salt and compound sodium chloride injection to ensure the safety use of salt is significant. The main methods for determination of K^+ include gravimetry[1,2], volumetry[3], Flame photometer method[4], ICP-AES[5,6], turbidimetry[7-9], Flame atomic absorption spectrometry[10-14], electro-analysis[15-19], solvent extraction spectrophotometry[20], ion chromatography[21], X (γ) - ray analysis[22-25] and so on. These methods have their own characteristics, but there are still failings for each other. In which sodium tetraphenylborate gravimetric and volumetric methods can only be used to determine the samples of relatively high potassium content. The gravimetric method is accurate, but the operation is more complicated and time-consuming, can not provide timely results. The volumetric method is simple, quick, but without high accuracy and unable for the determination of trace potassium. Turbidimetry, flame photometer, ICP-AES, flame atomic absorption spectrometry, electro-analysis and other methods use for determination of trace potassium, but can only be used for determination the samples with low matrix elements. When these methods were used for the determination trace potassium of concentration salt solution, the result was unsatisfactory, because there were a lot of matrix elements, which interfered seriously the determination of trace potassium.

The goal of this study was to solve the matrix elements interference issues of determination of trace potassium in concentrated salt solution. In the present work, the fluorescence spectral properties of K^+- rhodamine B-sodium tetraphenylborate system were studied. A new method for determination of trace potassium in concentration salt solution by anti-fluorescence quenching method on Rhodamine B-sodium Tetraphenylborate system was proposed. The expected advantages of this method are simple, fast, sensitive, low cost, the higher repeatability and with no interference from matrix

elements and in the presence of a large number of sodium ions, the trace potassium can be measured accurately. The method has been successfully used for the determination of trace potassium in common salt and compound sodium chloride injection with satisfactory results.

EXPERIMENTAL

All measurements were carried out using RF-5301 PC fluorescence spectrophotometer (Shimadzu Corporation, Japan) and 970 CRT fluorescence spectrophotometer (Shanghai Third Instrument Factory, China) with 375 nm for excitation wavelength and 640 nm for emission wavelength. The slit width was 10 nm.

All solutions were prepared using non-ionized water and analytical grade quality reagents. Potassium stock solution (0.01 mol L^{-1}) was obtained by dissolving 0.1864 g KCl (Chemical Plant of Changshu, China) (KCl was dried previously at 110 °C) in non-ionized water and diluting to a final volume of 250 mL. The Rhodamine B stock solution (0.01 mol L^{-1}) was prepared by dissolving 1.1976 g Rhodamine B (RhB, Guangdong Chemical Reagent Factory, China) in non-ionized water and diluting to a final volume of 250 mL. The sodium tetraphenylborate (NaTPB, Chemical Co. Ltd. Shanghai Shen Bo, China) stock solution (0.01 mol L^{-1}) was prepared by pharmacopoeia method[26]. Working solutions were prepared by appropriate dilution of the stock solution with non-ionized water.

2.50 mL 5.0×10^{-3} mol L^{-1} sodium tetraphenyl borate solutions and a certain amount of KCl solutions were added in sequence to a 10 mL colourimetric tube, mixed well and reacted for 5 min. Then 2.70 mL 5.0×10^{-3} mol L^{-1} RhB solutions were added, diluted to the mark with non-ionized water and mixed well. The mixture solution was placed in a constant temperature water bath for 30 min at 25 °C. Then the solution's fluorescence intensity F_1 was measured with 375 nm for excitation wavelength and 640 nm for emission wavelength. The fluorescence intensity of blank solution F_0 was measured under the same conditions, calculated the $\Delta F = F_1 - F_0$.

Method principle: In the aqueous solution sodium tetraphenylborate with a negative charge after dissociating of a Na$^+$, rhodamine B with a positive charge after dissociating of a Cl$^-$, they associated by 1:1. The anthraquinone π-bond electron distribution of rhodamine B was changed, so that fluorescence quenching of rhodamine B. Then, K$^+$ combined with sodium tetraphenylborate form more stable 1:1 association complex, the re-release of rhodamine B, enhanced fluorescence intensity of the solution. The principle of the method was as follows:

A + B = AB (Fluorescence quenching)

AB + C = BC + A (Anti-fluorescence quenching)

Marked: A-RhB, B-NaTPB, C-K$^+$

We can see from the above described mechanism that as the K$^+$ concentration increased, the anti-quenching effect were stronger. The fluorescence intensity of re-released was proportional to the concentration of K$^+$. Accordingly, a new, simple and sensitive antifluorescence quenching method for determination of K$^+$ was established.

RESULTS AND DISCUSSION

Spectra of antifluorescence quenching: The emission wavelength range of rhodamine B is generally 560-660 nm, as the concentration increased, the emission peak wavelength red-shift, which is caused due to self absorption (Fig. 1). Solvent effects also have an impact on fluorescence properties of rhodamine B. This effect can be considered as caused by the solvent polarity. The polarity of the electronic excited state of rhodamine B is larger than the ground state, as the increase of solvent polarity, fluorescence emission gradually transition to the state of relaxation and λ_{em} redshift[27,28]. After adding sodium tetraphenyl borate which has a certain polarity, solvent polarity was enhanced. This explained the spectra above that why added the sodium tetraphenyl borate, quenched part fluorescence of rhodamine B, the fluorescence emission wavelength of residual rhodamine B was red shifted.
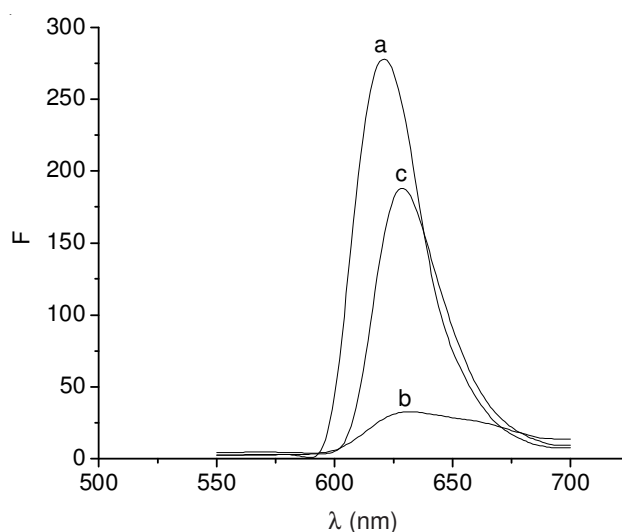

Fig. 1. Spectra of antifluorescence quenching; a: RhB (1.35×10^{-3} mol L^{-1}); b: a + NaTPB (1.25×10^{-3} mol L^{-1}); c: b + K$^+$ (1.0×10^{-3} mol L^{-1})

Fluorescence spectra of different concentration solution: Fig. 2 showed that with increasing the concentration of KCl solution, the antiquenching effect on Rhodamine B-sodium tetraphenylborate system was enhanced and the fluorescence intensity of the system was increased. In this paper, we determined quantitatively potassium ion just based on this principle.

Effect of pH: In accordance with the experimental method, fixed the other conditions, the effects of pH on the ΔF value of solution system was studied by adding a certain amount of HCl solutions (0.1 mol L^{-1}) and NaOH solutions (0.1 mol L^{-1}). The results was shown in Fig. 3. It was found that the ΔF of solution system without HCl solution and NaOH solution, pH = 6, was maximum.

Effect of reaction temperature: According to the experimental method, fixed other conditions, the effect of reaction temperature on the value of ΔF was studied by changing the temperature in the range of 15-60 °C. As Fig. 4 shown, it was found that when the temperature was lower than 25 °C, with the temperature increasing, the value of ΔF was greater. The value of ΔF was maximum at 25 °C. Above 25 °C, the value of ΔF was reduced with the temperature increasing. Thus with
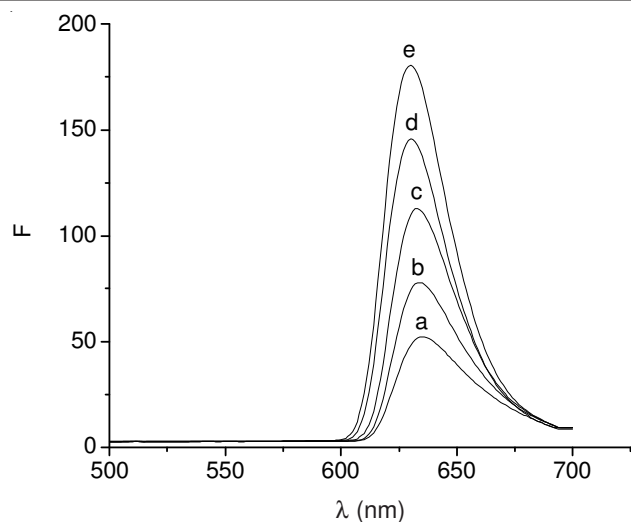
Fig. 2. Fluorescence spectra of different concentration range; a: NaTPB (1.25×10^{-3} mol L^{-1})-RhB (1.35×10^{-3} mol L^{-1}) -K + (11.73 mg L^{-1}); b: NaTPB (1.25×10^{-3} mol L^{-1}) -RhB (1.35×10^{-3} mol L^{-1}) -K^+ (17.59 mg L^{-1}); c: NaTPB (1.25×10^{-3} mol L^{-1}) -RhB (1.35×10^{-3} mol L^{-1}) -K^+ (23.46 mg L^{-1}); d: NaTPB (1.25×10^{-3} mol L^{-1}) -RhB (1.35×10^{-3} mol L^{-1}) -K^+ (29.32 mg L^{-1}); e: Na TPB (1.25×10^{-3} mol L^{-1}) -RhB (1.35×10^{-3} mol L^{-1}) -K^+ (35.19 mg L^{-1})
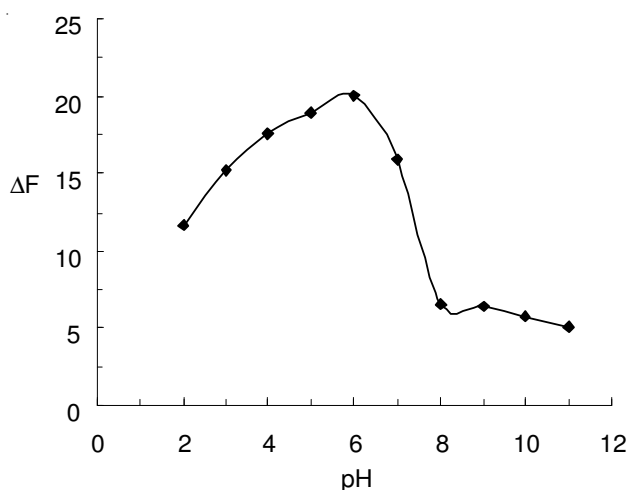

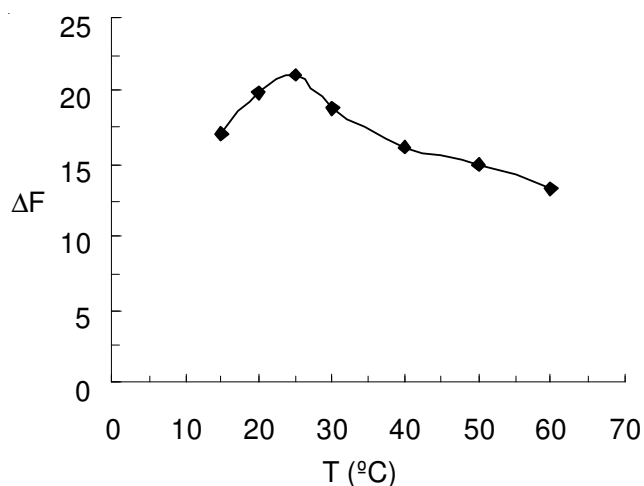Fig. 3. Influence of acidity on ΔF

Fig. 4. Influence of temperature on ΔF

increasing temperature, the complex of K^+ and sodium tetraphenylborate association was dissociated so that the anti-fluorescence quenching effect of K^+ on the system was weakened. Therefore, in this experiment, we chose 25 ºC for the optimum temperature.

Effect of reaction time: According to the experimental method, fixed other conditions, put the solution in a constant temperature water bath at 25 ºC, the value of ΔF was measured between different time, studied the effect of reaction time on the value of ΔF. The results was shown in Fig. 5. The value of ΔF slowly increased with the reaction time increasing. When over 30 min, the reaction was completed, the value of ΔF stabilized. In this study, we taken the best time of 30 min.
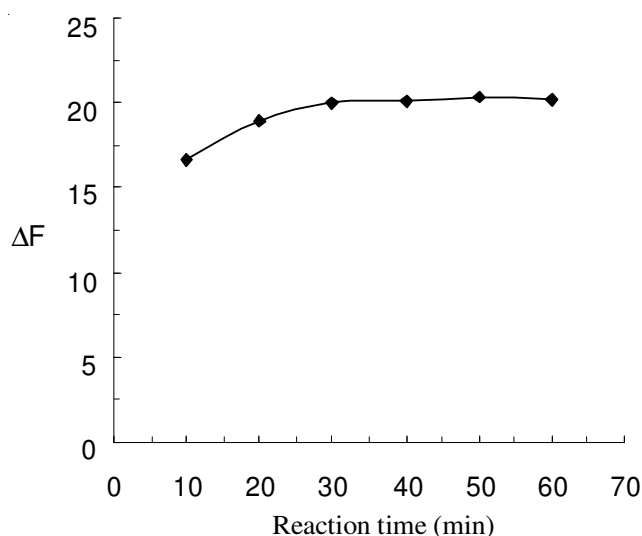

Fig. 5. Influence of reaction time on ΔF

Effect of amount of rhodamine B: 2.50 mL 5.0×10^{-3} mol L^{-1} sodium tetraphenyl borate solutions and 2.0 mL 5.0×10^{-3} mol L^{-1} KCl solutions were added respectively in six volumetric flasks of 10 mL, mixed well. After reacting for 5 min, 2.50 mL, 2.60 mL, 2.70 mL, 2.80 mL, 2.90 mL, 3.00 mL 5.0×10^{-3} mol L^{-1} rhodamine B solutions were added respectively, mixed well and the solutions were diluted to the mark with non-ionized water. They were placed in 25 ºC water bath pot for 30 min. Then the solutions' fluorescence intensity F_1 was measured with 375 nm for excitation wavelength and 640 nm for emission wavelength. The fluorescence intensity F_0 of blank solution was measured under the same conditions, calculated the ΔF (ΔF = F_1-F_0). The results was shown in Fig. 6. The figure indicated that beginning the value of ΔF was increased gradually with the increase in the amount of rhodamine B and reached the maximum when rhodamine B was 2.70 mL, then to continue to increase the amount of rhodamine B, it was decreased. So, the best proportion of sodium tetraphenyl borate, rhodamine B and K^+ should be controlled at 2.5 : 2.7 : ≤ 2.

Calibration curve: Under the selected optimum conditions, fixed amount of other solutions, changed the amount of KCl standard solution, a series of reaction solution were prepared. In accordance with the test method, ΔF of the solution were measured. A standard curve was obtained by taking ΔF for the ordinate and the mass concentration of K^+ m
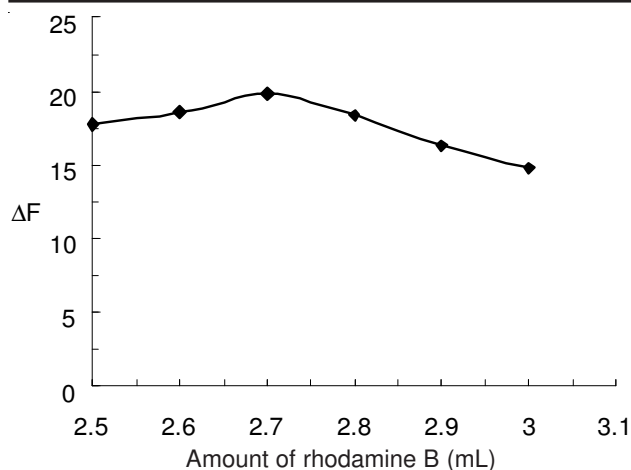
Fig. 6. Best amount of rhodamine B

(mg/L) for the abscissa. The regression equation was $\Delta F = 0.6969 m - 3.2708$ with the correlation coefficient R of 0.9989. The results indicated that ΔF and the concentration of K^+ showed a good linear relationship in the range of 2.14 mg L^{-1}- 43.0 mg L^{-1}. The detection limit (3σ) obtained by IUPAC regulations was 0.642 mg L^{-1}. Prepared the same concentration of test solution of 11 in accordance with the experimental method and measured the ΔF of 11, the RSD of the data was 1.32 %, showing good precision of the method.

Interference: Under the optimum conditions, the interference of components, which may be added in common salt and compound sodium chloride injection was investigated by measuring solutions containing 1.0×10^{-3} mol L^{-1} of K^+ and interfering compounds with various concentration. Based on the impact of the fluorescence intensity was not more than ± 5 %, the largest allowable amount of foreign substances was ranged 50-200.

The results showed that 200 times Na^+, Zn^{2+}; 100 times Ba^{2+}, SO_4^{2-}, CO_3^{2-}, ClO_3^-; 50 times Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, NO_3^-, $H_2PO_4^-$ had no interferences on the determination results (Table-1). Since the actual content of these substances in samples were lower than the allowable maximum amount of content, so the samples can be determined directly without additional pretreatment or separation. NH_4^+ can react with sodium tetraphenylborate to form white precipitate, which had

great impact on the experimental results. If there were NH_4^+ in samples, we must try to remove it to avoid interference on the determination. However, rarely contained NH_4^+ in common salt and compound sodium chloride injection, the interference of NH_4^+ was not discussed in this paper.

TABLE-1
RESULTS OF INTERFERENCE EXPERIMENT

Name of interferences	Maximum times allowed	Name of interferences	Maximum times allowed
Na^+	200	Ba^{2+}	100
Ca^{2+}	50	SO_4^{2-}	100
Mg^{2+}	50	CO_3^{2-}	100
Al^{3+}	50	ClO_3^-	100
Zn^{2+}	200	NO_3^-	50
Fe^{2+}	50	$H_2PO_4^-$	50

Determination of samples

Preparation of sample solution: Sample solution of sodium salt: 1.2500 g sample of low sodium salt was weighed, dissolved and diluted to 250 mL with non-ionized water, mixed well. This solution was diluted to 10 times to be used test solution.

Sample solution of sea salt was obtained by dissolving 3.0000 g sea salt samples in non-ionized water and diluting to the mark in a 100 mL volumetric flask.

Sample solution of compound sodium chloride injection: 50 mL of compound sodium chloride injection samples was placed into a 100 mL volumetric flask, diluted to the mark with non-ionized water, mixed well.

Determination and recovery of samples: According to the procedure, the 2.00 mL prepared sample solution was used to determine the K^+ content of the sample of salt and compound sodium chloride injection of different manufacturers. In order to detect the reliability of the determination method, the recovery tests are carried out. The results were shown in Table-2.

Comparison: In order to further test the accuracy of the method, the determination of potassium in low sodium by anti-fluorescence quenching method and the pharmacopoeia method (gravimetric method)[16] and two methods results were compared. The results shown in Table-3.

The results of two methods were analyzed by t-test method. As the *t*-value of two methods results is 1.35, *t* = 1.35

TABLE-2
RESULTS OF RECOVERY TEST FOR THE DETERMINATION OF SAMPLES

Sample	Average of determination (mg)	RSD /% (n=5)	Added (mg)	Measured value (mg)	Recovery (%)	RSD /% (n = 5)
1	0.1376	0.48	0.09775	0.2357	100.4	1.7
			0.1368	0.2767	101.7	2.0
2	0.03107	1.9	0.03910	0.06886	96.65	1.7
			0.01955	0.04982	95.91	0.25
3	0.1554	1.6	0.07820	0.2341	100.6	1.5
			0.1173	0.2686	96.50	1.6
4	0.1584	1.6	0.07820	0.2385	102.4	1.4
			0.1173	0.2722	97.00	1.2
5	0.1581	1.2	0.07820	0.2399	104.6	1.3
			0.1173	0.2757	100.3	0.95

Sample 1: Low sodium (Salt Co. Ltd. Guangxi Beihai iodized salt centre produced)
Sample 2: Sea salt (Guangdong Province, the company of varieties of salt produced)
Sample 3: Compound sodium chloride injection (Music echo Asia Group Pharmaceutical Co. Ltd., Jiangxi)
Sample 4: Compound sodium chloride injection (Four Shijiazhuang Pharmaceutical Co. Ltd.)
Sample 5: Compound sodium chloride injection (Pharmaceutical Co. Ltd. Hunan Cogent)

TABLE-3
CONTRAST OF DIFFERENT EXPERIMENTAL
METHOD RESULTS

Method	Determination results (%)	RSD/% (n = 5)	Different value between the methods (%)
Anti-fluorescence quenching	13.76	0.48	+ 0.04
Gravimetry	13.72	0.67	

$< t$ $t_{0.05,4} = 2.78$, therefore, there were no significant difference between new methods and pharmacopoeia method in $\alpha = 0.05$ level.

Conclusion

Compared with the classical gravimetric method, the new method of determination of trace potassium established by anti-fluorescence quenching on rhodamine B-sodium tetraphenyl borate system is the same accuracy, but higher sensitivity, better select and faster measuring. The simple and inexpensive instrumentation and easy manipulation are valuable characteristics of this method. It can be used for determination of trace potassium in high concentration salt solution without the interference of matrix elements of sodium and make up the defects of gravimetric method which is time-consuming, cumbersome and greatly reducing the testing cycle. The new method also overcome the shortcoming of atomic spectrometry that can not truly determine trace potassium in high concentration salt solution.

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